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Thermodynamic Properties of Micellization of Sodium Dodecylbenzene Sulfonate in the Aqueous-Rich Region of 1-Pentanol and 1-Hexanol

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Apparent molar volumes, Φv, and isentropic compressibilities, κ_s, of the aqueous solutions of anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), have been derived from experimental densities, ρ, and speed of sound, u, data measured below 0.40 $\text{mol}\cdot\text{kg}^{-1}$ at $T = (298.15, 303.15, 308.15, \text{and } 313.15)$ K using an Anton Paar densimeter (DSA-5000). Conductance measurements were also made for aqueous solutions of SDBS to obtain critical micelle concentration at the above temperatures. Apparent molar volumes and isentropic compressibilities of 1-pentanol and 1-hexanol dissolved in aqueous micellar solutions of SDBS were determined as a function of molalities of surfactant (0.05 and 0.1) $\text{mol}\cdot\text{kg}^{-1}$ and alcohols at $T = (298.15 \text{ and } 308.15)$ K. The standard partial molar volumes, $\Phi^{\text{o}}v$, and transfer volume, $\Phi^{\text{o}}v_{(\text{tr})}$, have been calculated for rationalizing various interactions in the studied solutions. Viscosity measurements were made for the above-mentioned alcohols in aqueous solutions of SDBS to obtain relative viscosity and viscosity *B*-coefficient. The second transition of aqueous sodium dodecylbenzene sulfonate in the postmicellar region has been obtained. Proton NMR chemical shift measurements in micelle solutions containing 1-pentanol have also been made, the results of which support the conclusions drawn from thermodynamic measurements.

Introduction

An important feature of micellar systems is their ability to accommodate a large amount of organic compounds which are otherwise sparingly soluble or insoluble in water.[1] By adding neutral salt and a medium chain alcohol in a micellar system, the ability to solubilize hydrophobic molecules can be improved.[2] Therefore these components are used in most microemultions.[3,4] The size and shape of micelle aggregates containing commonly used surfactant and cosurfactant have been critically examined.[5,6] Micellar solubilization is important for many technical applications such as in pharmaceuticals, polymerization processes, detergency, foods, and enhanced oil recovery. The solubilization of aliphatic alcohols in micelles is one of the aspects of this phenomenon which has been studied by means of various techniques.[7]

Sodium dodecylbenzene sulfonate, SDBS, is an anionic surfactant which is used in chemical, biochemical, and industrial works. The solution properties of this surfactant have not been critically examined although several papers are available in the literature.[8−14] Hait et al.[8] studied the micellization process of SDBS and its interaction with neutral and cationic polymers by various methods. Alauddin et al.[9] discussed the volumetric, adiabatic compressibility, and NMR studies of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2- or 3-*tert*-butyl-4-methoxyphenol (BHA) in aqueous micelle solution of SDBS above the critical micelle concentration. Bakshi et al.[10] studied SDS + SDBS mixed micelle formation in the presence of water-soluble polymers using various physicochemical techniques. Saiyad et al.[11] discussed various physicochemical properties of mixed surfactant SDBS + TritonX 100 at different temperatures. While the reports on the interaction of sodium dodecylsulfate, SDS, with alcohols are considerable,[15−19] that with SDBS is nil.

With this background, the objective of the present study is to investigate the micellization of SDBS in aqueous solution and its interactions with medium chain alcohols, 1-pentanol and 1-hexanol, critically. The process of micellization of SDBS in the aqueous phase has been assessed by the apparent molar volume Φv, partial molar volume $\Phi^{\text{o}}v$, transfer volume $\Phi^{\text{o}}v_{(\text{tr})}$, isentropic compressibility κ_s, and viscosity *B*-coefficients, calculated from the experimental data of density, ρ, speed of sound, u, and viscosity, η, of alcohols, 1-pentanol at $m = (0.05$ to $0.25)$ $\text{mol}\cdot\text{kg}^{-1}$, and 1-hexanol at $m = (0.01$ to $0.08)$ $\text{mol}\cdot\text{kg}^{-1}$ in $m = (0.05$ and $0.10)$ $\text{mol}\cdot\text{kg}^{-1}$ aqueous SDBS solutions at (298.15 and 308.15) K. Further, the ^{1}H NMR studies have also been done, the results of which are interpreted in terms of the approximate location of the alcohols in the micellar aggregates. Possible changes in the shape and size of the micelles along with the interactions within the micelle between the alcohols and surfactant species have also been made. Various thermodynamic parameters for the studied aqueous SDBS solutions suggest that SDBS micelles undergo a second transition at higher surfactant concentration. An exhaustive survey of the literature reveals that no one has reported such an extensive study of aqueous micelle solution of SDBS above the critical micelle concentration, containing monohydric medium chain alcohols using simple thermodynamic properties.

Experimental Section

Materials. Sodium dodecylbenzene sulfonate (SDBS) of stated purity 88 % was purchased by Acros Organics (New Jersey). It was purified by the method given in the literature.[9] The purified product was dried under vacuum in the presence of P_2O_5 for a few days. The expected purity of the recrystallized SDBS was > 97 % as checked by comparing the data of critical micelle concentrations of aqueous SDBS given by Hait et al.[8] The experimental values of speed of sound at 298.15 K for aqueous SDBS were compared with that reported in the

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Table 1. Comparison of Experimental Density, ρ, Speed of Sound, u, and Viscosity, η, of Pure Liquids with Literature Data

		$\rho \cdot 10^{-3}$ $\mathrm{kg \cdot m^{-3}}$		$u/\mathrm{m \cdot s^{-1}}$		$\eta/\mathrm{mPa \cdot s}$	
alcohols	T/K	exptl	lit.	exptl	lit.	exptl	lit.
1-pentanol	298.15	0.810972	0.8109[20]	1275.21	1276.0[20]	3.515	3.513[25]
	308.15	0.803552	0.8034[21]	1241.84	–	2.380	2.305[25]
1-hexanol	298.15	0.815343	0.8153[22]	1304.67	1304.7[23]	4.596	4.492[25]
	308.15	0.808331	0.8084[24]	1271.23	1271.1[23]	3.270	3.252[24]

literature.[9] The analytical grade 1-pentanol 99 % (Spectrochem Pvt Ltd. Mumbai, India) and 1-hexanol 98 % (Acros Organics, New Jersey) were purified by fractional distillation before use. The purity of these liquids was ascertained by comparing their measured densities, ρ, speeds of sound, u, and viscosities, η, with those reported in the literature.[20−25] The determined densities and speeds of sound of pure components agree with the literature data very well and are given in Table 1. Deuterium oxide (Aldrich, 99.9 % isotopic purity) was used without further purification as solvent in ^{1}H NMR studies. Deionized, double distilled water of conductance $1 \cdot 10^{-6}$ S·cm^{-1} at 298.15 K was used for all measurements. Solutions were prepared by weighing an appropriate amount of the SDBS on an electronic balance, (Afcoset-ER120A) with a precision of 0.0001 g. Bidistilled water and alcohols were degassed by a vacuum pump shortly before sample preparation.

Apparatus and Procedure. Measurements of the density, ρ, and the speed of sound, u, of pure liquids and their solutions were carried out using a digital vibrating tube densimeter and speed of sound analyzer (Anton Paar DSA-5000) provided with automatic viscosity correction and two integrated Pt 100 thermometers. The temperature in the cell was regulated ± 0.001 K with a proportional temperature controller. The apparatus was first calibrated with triple distilled water and dry air. The uncertainties in density measurements were estimated to be ± $2 \cdot 10^{-3}$ kg·m^{-3} and for the speed of sound ± 0.1 m·s^{-1}. Further information about the experimental techniques has been provided in our previous work.[26]

The kinematic viscosities of the pure liquids and their mixtures were measured at (298.15 and 308.15) K and atmospheric pressure using an Ubbelohde suspended level viscometer. Experimental details have been given previously.[26,27] The viscometer was filled with liquid or liquid mixtures, and its limbs were closed with Teflon caps taking due precaution to reduce evaporation losses. An electronic digital stopwatch with a readability of 0.01 s was used for flow time measurements. Experiments were repeated a minimum of four times for all compositions, and the results were averaged. The caps of the limbs were removed during the measurement of flow times. The measured values of kinematic viscosity, ν, were converted to dynamic viscosity, η, after multiplication by the density. The reproducibility of dynamic viscosity was found to be within ± 0.003 mPa·s. A thermostatically controlled, well-stirred water bath whose temperature was controlled to ± 0.01 K was used for all the measurements.

Conductivity measurements were carried out in a jacket containing a conductivity cell of cell constant 1.0 cm^{-1}. Water was circulated in the jacket from thermostat, and the temperature was maintained within ± 0.01 K. The critical micelle concentration, cmc, of SDBS in an aqueous solution was taken as the break point in the plot of specific conductance vs molar concentration (mol·dm^{-3}) of SDBS. The cmc of SDBS in water was determined to be 2.58 mmol·dm^{-3} at 298.15 K and was found to be in good agreement with the value reported in the literature[2] (2.9 mmol·dm^{-3}), whereas at T = (303.15, 308.15, and 313.15) K it was (2.75, 2.80, and 3.05) mmol·dm^{-3}, respectively, and showed agreement with literature values measured by different techniques.[8]

To investigate the effect of alcohols on the micellar phase, ^{1}H NMR measurements were performed on an Avance II 400 NMR spectrometer at a frequency of 400.13 MHz. Deuterium oxide was used as the solvent instead of water to weaken the water signal for all solutions. The method depends on the ability of the alcohols to affect the chemical shift of different proton signals of the surfactant molecules. These chemical shifts were measured in the presence of solubilizate, 1-pentanol, as a function of both alcohol and surfactant concentrations. The surfactant concentrations are always kept higher than the cmc for the NMR studies. The chemical shift differences were only considered in this study. The chemical shift measurements of various resonance peaks of SDBS are given on the δ scale in parts per million (ppm) of the applied frequency.

Results and Discussion

The experimental data of density (ρ), speed of sound (u), and viscosity (η) along with the apparent molar volume (Φv) and isentropic compressibility (κ_s) of 1-pentanol and 1-hexanol in aqueous solutions of SDBS at (298.15 and 308.15) K and atmospheric pressure are reported in Table 2. The uncertainty reported in density measurements is ± $2 \cdot 10^{-3}$ kg·m^{-3} and in speed of sound is ± 0.1 m·s^{-1}. Figures 1 and 2 show the concentration dependence of conductivity and speed of sound, respectively, of aqueous solution of SDBS in its micellar range at T = (298.15, 303.15, 308.15, and 313.15) K. In Figure 1, the cmc of aqueous SDBS solution was taken as the break point in the plot of specific conductance vs molal concentration of aqueous SDBS. In Figure 2, a gradual change is seen at very low concentrations which are apparent at higher temperatures also.

The apparent molar volumes (Φv) for aqueous surfactant solutions and that with alcohols can be calculated from the density using the following expression

$$\Phi v = (M/\rho) - [\{1000(\rho_o - \rho)\}/m\rho\rho_o] \tag{1}$$

where ρ_o, M, and m are, respectively, the density of the pure solvent (aqueous SDBS), the molar mass of the solute, and the molality (mol·kg^{-1}) of the solute (alcohols). The values of Φv for alcohols at infinite dilution were determined by using the least-squares method to fit the low concentration data to the assumed relation

$$\Phi v = \Phi^o v + S_v m \tag{2}$$

where the intercept $\Phi^o v$ by definition is free from solute−solute interactions and therefore provides a measure of solute−solvent interaction, whereas the experimental slope S_v provides information regarding solute−solute interactions[28] and was obtained by using linear regression of Φv vs molality from eq 2. The values of $\Phi^o v$ and S_v along with the standard deviations for both the alcohols at T = (298.15 and 308.15) K are listed in Table 3.

The thermodynamic transfer functions may be interpreted in terms of structure making or breaking effects of the solute.[6] The volume of transfer of 1-pentanol or 1-hexanol from water to aqueous surfactant, $\Phi^o v_{(\mathrm{tr})}$, was calculated by using the relation

$$\Phi^o v_{(\mathrm{tr})} = \Phi^o v(\text{in aqueous surfactant}) - \Phi^o v(\text{in water}) \tag{3}$$

where $\Phi^o v$ (in water) is the partial molar volume of the alcohols in water and its values at 298.15 K have been taken from the

Table 2. Density, ρ, Apparent Molar Volume, Φv, Speed of Sound, u, Isentropic Compressibility, κ_s, and Viscosity, η, of 1-Pentanol or 1-Hexanol in Aqueous Sodium Dodecylbenzene Sulfonate Solutions at (298.15 and 308.15) K

m	$\rho\cdot10^{-3}$	Φv	u	$\kappa_s\cdot10^{10}$	η
mol·kg^{-1}	kg·m^{-3}	cm^3·mol^{-1}	m·s^{-1}	Pa^{-1}	mPa·s
1-pentanol			SDBS (0.05 mol·kg^{-1})		
			298.15 K		
0.000	0.999920	–	1498.7	4.4525	0.999
0.058	0.999100	102.30	1501.01	4.4425	1.035
0.089	0.998650	102.63	1502.02	4.4385	1.050
0.109	0.998330	102.88	1502.83	4.4351	1.064
0.144	0.997784	103.24	1503.80	4.4319	1.078
0.191	0.997025	103.60	1505.46	4.4254	1.098
0.220	0.996525	103.91	1506.20	4.4233	1.112
0.236	0.996260	104.06	1506.60	4.4221	1.120
0.255	0.995850	104.23	1507.20	4.4202	1.128
			308.15 K		
0.000	0.996760	–	1522.67	4.3271	0.795
0.058	0.995955	102.41	1523.8	4.3242	0.821
0.089	0.995485	103.06	1524.58	4.3218	0.829
0.109	0.995157	103.37	1525.13	4.3201	0.838
0.144	0.994600	103.78	1525.77	4.3189	0.853
0.191	0.993780	104.43	1526.68	4.3173	0.866
0.220	0.993238	104.89	1527.12	4.3172	0.876
0.236	0.992970	105.03	1527.14	4.3182	0.879
0.255	0.992630	105.25	1527.18	4.3196	0.881
			SDBS (0.1 mol·kg^{-1})		
			298.15 K		
0.000	1.002755	–	1500.00	4.4322	1.106
0.092	1.001389	102.81	1502.92	4.4211	1.148
0.123	1.000896	103.10	1503.63	4.4191	1.172
0.125	1.000875	103.11	1503.71	4.4187	1.171
0.181	0.999971	103.51	1504.8	4.4163	1.222
0.234	0.999102	103.80	1505.80	4.1425	1.291
0.276	0.998380	104.11	1506.49	4.4134	1.358
0.296	0.998048	104.20	1506.87	4.4126	1.381
			308.15 K		
0.000	0.999440	–	1523.45	4.3111	0.868
0.092	0.998081	103.20	1524.44	4.3114	0.899
0.123	0.997610	103.35	1524.67	4.3121	0.918
0.125	0.997591	103.40	1524.71	4.3120	0.921
0.181	0.996680	103.81	1525.32	4.3125	0.958
0.234	0.995771	104.27	1525.36	4.3162	1.000
0.276	0.995041	104.60	1525.71	4.3173	1.046
0.296	0.994691	104.74	1525.79	4.3184	1.067
1-hexanol			SDBS (0.05 mol·kg^{-1})		
			298.15 K		
0.000	0.999920	–	1498.70	4.4525	0.999
0.01	0.999764	117.80	1498.35	4.4553	1.000
0.02	0.999605	117.97	1498.10	4.4575	1.005
0.03	0.999443	118.14	1497.85	4.4597	1.011
0.04	0.999278	118.31	1497.55	4.4622	1.018
0.046	0.999178	118.40	1497.35	4.4639	1.020
0.06	0.998937	118.68	1496.90	4.4676	1.035
0.067	0.998810	118.88	1496.70	4.4694	1.041
0.08	0.99858	119.09	1496.38	4.4723	1.060
			308.15 K		
0.000	0.996760	–	1522.67	4.3271	0.795
0.01	0.996607	117.92	1522.5	4.3287	0.799
0.02	0.996451	118.08	1522.32	4.3304	0.800
0.03	0.996292	118.26	1522.15	4.3321	0.802
0.04	0.996131	118.41	1522.00	4.3337	0.803
0.046	0.996033	118.50	1521.92	4.3345	0.804
0.06	0.995794	118.83	1521.70	4.3368	0.806
0.067	0.995670	119.01	1521.60	4.3379	0.808
0.08	0.995440	119.27	1521.40	4.3401	0.809
			SDBS (0.1 mol·kg^{-1})		
			298.15 K		
0.000	1.002755	–	1500.00	4.4322	1.060
0.01	1.002593	118.00	1499.76	4.4344	1.108
0.02	1.002429	118.14	1499.47	4.4368	1.109
0.03	1.002262	118.31	1499.14	4.4395	1.110
0.04	1.002090	118.51	1498.84	4.4420	1.112
0.05	1.001914	118.72	1498.45	4.4451	1.115
0.06	1.001731	118.99	1498.12	4.4479	1.118
0.065	1.001640	119.08	1497.91	4.4496	1.121
0.075	1.001455	119.29	1497.60	4.4522	1.126
0.08	1.001364	119.35	1497.38	4.4539	1.130
			308.15 K		
0.000	0.999440	–	1523.45	4.3111	0.868
0.01	0.999282	118.06	1523.16	4.3134	0.868
0.02	0.999122	118.19	1522.80	4.3161	0.869
0.03	0.998957	118.42	1522.50	4.3186	0.869
0.04	0.998790	118.58	1522.25	4.3207	0.870
0.05	0.998616	118.83	1522.02	4.3228	0.871
0.06	0.998440	119.04	1521.76	4.3250	0.873
0.065	0.998352	119.12	1521.61	4.3262	0.873
0.075	0.998173	119.29	1521.36	4.3284	0.876
0.08	0.998081	119.40	1521.22	4.3296	0.880

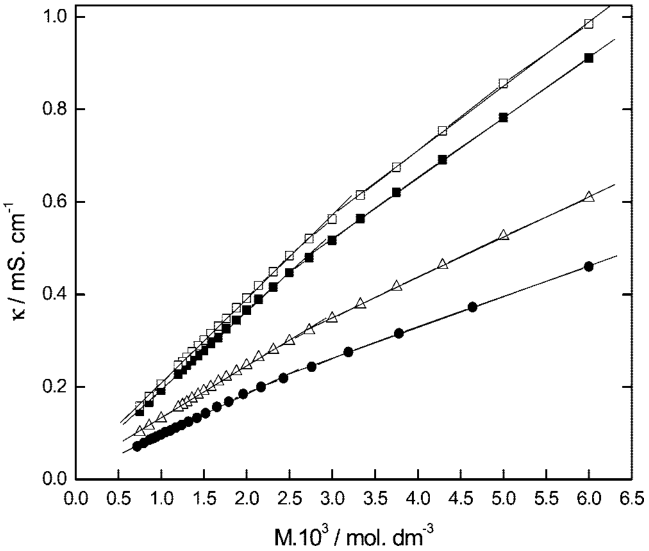

Figure 1. Conductivity, κ, of aqueous solutions of SDBS as a function of molarity: ●, 298.15 K; Δ, 303.15 K; ■, 308.15 K; and □, 313.15 K.

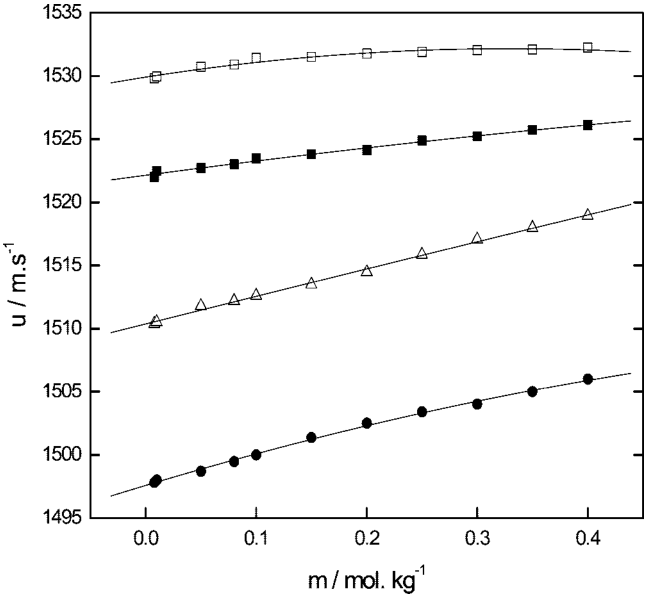

Figure 2. Speed of sound, u, in aqueous solutions of SDBS as a function of molality: ●, 298.15 K; Δ, 303.15 K; ■, 308.15 K; and □, 313.15 K.

literature.[29] The $\Phi^{\circ}v_{(\mathrm{tr})}$ values at 298.15 K are summarized in Table 3.

The isentropic compressibility, κ_s, of the solution can be obtained by the Newton–Laplace equation

$$\kappa_s = (\rho u^2)^{-1} \tag{4}$$

The dynamic viscosities, η (reproducibility ± 0.003 mPa·s), of all the studied solutions at the same concentration as was used for the density and speed of sound measurements are listed in Table 2. The relative viscosity (η_{rel}) has been analyzed using the Jones–Dole equation[30]

$$\eta_{\mathrm{rel}} = \eta/\eta_{\mathrm{o}} = 1 + Am^{1/2} + Bm \tag{5}$$

where η and η_{o} are the viscosities of the ternary solutions (SDBS + water + alcohol) and binary solvents (SDBS +water), respectively, and m is the molal concentration of alcohols in ternary solutions. A and B are empirical constants known as viscosity A- and B-coefficients, which are specific to solute–solute

Table 3. Fit Coefficients of the Variation of Φv as a Function of the Concentration at (298.15 and 308.15) K for Aqueous−SDBS−Alcohol Solutions

alcohols	T / K	Φ°v / (cm³·mol⁻¹)	S_v / (cm³·mol⁻²·kg)	Φ°$v_{(water)}$ / (cm³·mol⁻¹)	Φ°$v_{(tr)}$ / (cm³·mol⁻¹)
		SDBS (0.05 mol·kg⁻¹)			
1-pentanol	298.15	101.83 ± 0.04[a]	9.45 ± 0.20	102.40[b]	−0.57
	308.15	101.91 ± 0.05	13.23 ± 0.25	−	−
		SDBS (0.1 mol·kg⁻¹)			
	298.15	102.26 ± 0.04	6.64 ± 0.21	102.40[b]	−0.14
	308.15	102.42 ± 0.04	7.84 ± 0.19	−	−
		SDBS (0.05 mol·kg⁻¹)			
1-hexanol	298.15	117.59 ± 0.03	18.67 ± 0.51	117.56[b]	0.03
	308.15	117.68 ± 0.04	19.36 ± 0.74	−	−
		SDBS (0.1 mol·kg⁻¹)			
	298.15	117.74 ± 0.03	20.27 ± 0.57	117.56[b]	0.18
	308.15	117.83 ± 0.02	19.65 ± 0.41	−	−

[a] Standard deviations. [b] Data taken from ref 29.

Table 4. Viscosity B-Coefficients of the Alcohols in Aqueous SDBS Solutions at T = (298.15 and 308.15) K

		B/dm³·mol⁻¹	
		SDBS	
	T/K	(0.05 mol·dm⁻³)	(0.1 mol·dm⁻³)
1-pentanol	298.15	0.391 ± 0.016	1.002 ± 0.054
	308.15	0.353 ± 0.031	1.001 ± 0.032
1-hexanol	298.15	0.915 ± 0.042	0.098 ± 0.051
	308.15	0.030 ± 0.029	0.091 ± 0.015

and solute−solvent interactions, respectively. Equation 5 can be rearranged as

$$n_{\text{rel}} - 1/m^{1/2} = A + Bm^{1/2} \qquad (6)$$

Values of A- and B-coefficients are obtained from a linear plot of the left-hand side of eq 6 vs $m^{1/2}$. The values of B-coefficients are listed in Table 4. Due to the complex nature of A-coefficients, they are not discussed in the present work.

The solubility of 1-pentanol in water, given in mass fraction, is w = 0.0219 at 25 °C, whereas that of 1-hexanol is 0.00706 at 20 °C.[25] The solubility of alcohols in SDBS micelle solutions increases with increase in molality of surfactant and temperature. However it was assumed that the solubility of these alcohols in water would not cause a significant change in the cmc of SDBS in water.

The plot of this study of Φv vs $m^{1/2}$ in the case of aqueous surfactant solutions show well-defined breaks at a surfactant concentration around 0.15 mol·kg⁻¹ (Figure 3). On increasing the temperature, the break appears to shift toward lower molal concentration. This may be explained by a decrease of counterion binding to the micelles which leads to an increase in intermicellar repulsive interaction. This repulsion favors a growth in micelle size at lower molal concentration to increase the intermicellar distances and to reduce the mutual repulsion. These results indicate that SDBS micelles apparently undergo a transition, probably sphere-to-rod at ≈ 0.15 mol·kg⁻¹. According to Allaudin et al.,[9] the increase of Φv of aqueous solutions of SDBS during transition in SDBS micelles can lead us to conclude that the counterions of SDBS aggregates may be tightly bound, and larger changes in Coulombic and structural hydration arise during the transition. It can be interpreted from the above discussion that the rod-shaped micelles of SDBS are less compact.

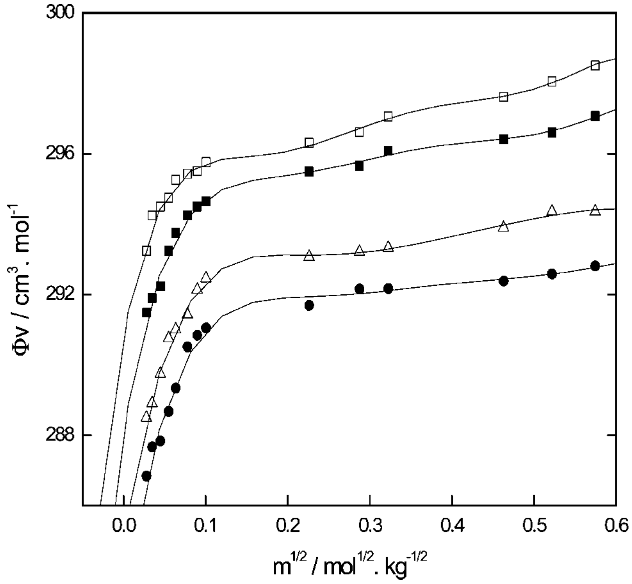

Figure 3. Apparent molar volume, Φv, of aqueous solutions of SDBS as a function of the square root of molality: ●, 298.15 K; Δ, 303.15 K; ■, 308.15 K; and □, 313.15 K.

The Φv values of 1-pentanol and 1-hexanol in aqueous micelle solution of SDBS at different molality and temperatures show that considerable variations occur in this property for the two alcohols (Figure 4). The plots of Φv vs molality of 1-pentanol at different surfactant concentrations in mol·kg⁻¹ and temperatures (Figure 4a) reveal that the variation of the apparent molar volume of 1-pentanol is nonlinear with molal concentration and that Φv is very much dependent upon the molalities of surfactant and alcohol as well as the temperature. The breaks that occur in the plot at certain alcohol concentrations reflect the fact that the shapes and size of the micelles are changing due to the presence of the 1-pentanol or maybe the alcohol molecules are changing location in the micellar aggregates. In the case of solutions containing 1-hexanol (Figure 4b), the plot of Φv vs alcohol concentration is linear at very low concentration of 1-hexanol.

The partial molar volume of a solute Φ°v reflects the true volume of the solute and the volume change arising from the solute−solvent interaction. It means that the change in Φ°v at different surfactant concentration and temperature should reflect the changes occurring in its environment in the micelle system. The value of Φ°v for 1-pentanol and 1-hexanol in different SDBS solutions shows that there is a significant difference between Φ°v for both the alcohols and that in aqueous data, indicating that the alcohol molecules are partly solubilized in the micelle solution of SDBS. A perusal of Table 3 indicates

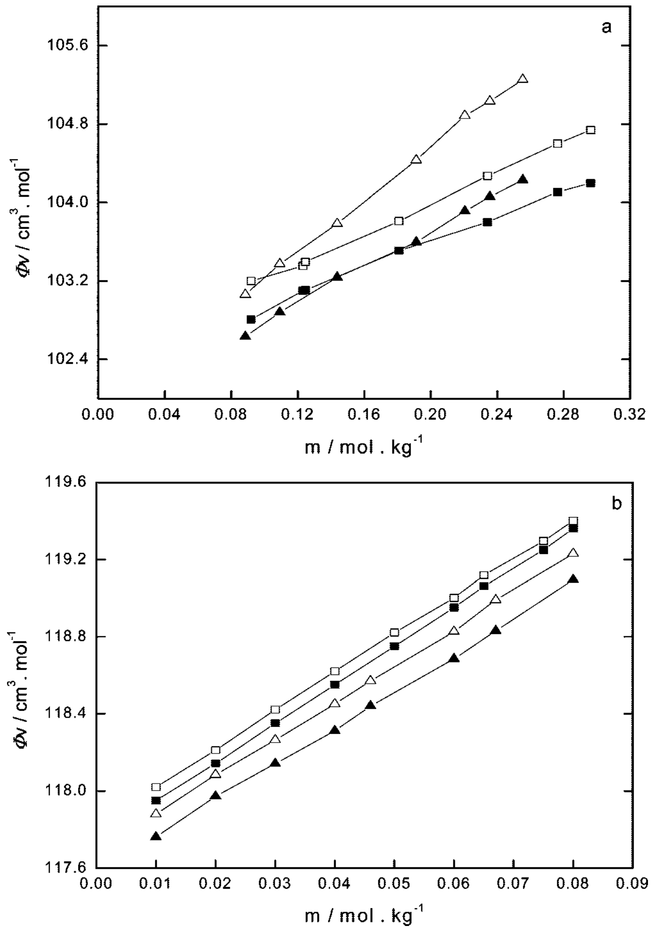

Figure 4. Apparent molar volume, Φv, of aqueous solutions of SDBS at different concentrations at 298.15 K: ▲, 0.05 mol·kg^{-1}; ■, 0.10 mol·kg^{-1}; and at 308.15 K: Δ, 0.05 mol·kg^{-1}; □, 0.10 mol·kg^{-1} with alcohols: (a) 1-pentanol and (b) 1-hexanol.

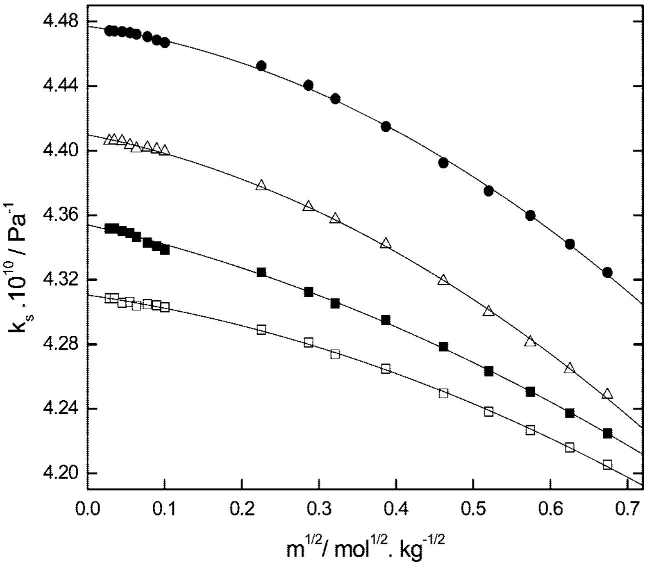

Figure 5. Isentropic compressibility, κ_s, of aqueous solutions of SDBS as a function of square root of molality: ●, 298.15 K; Δ, 303.15 K; ■, 308.15 K; and □, 313.15 K.

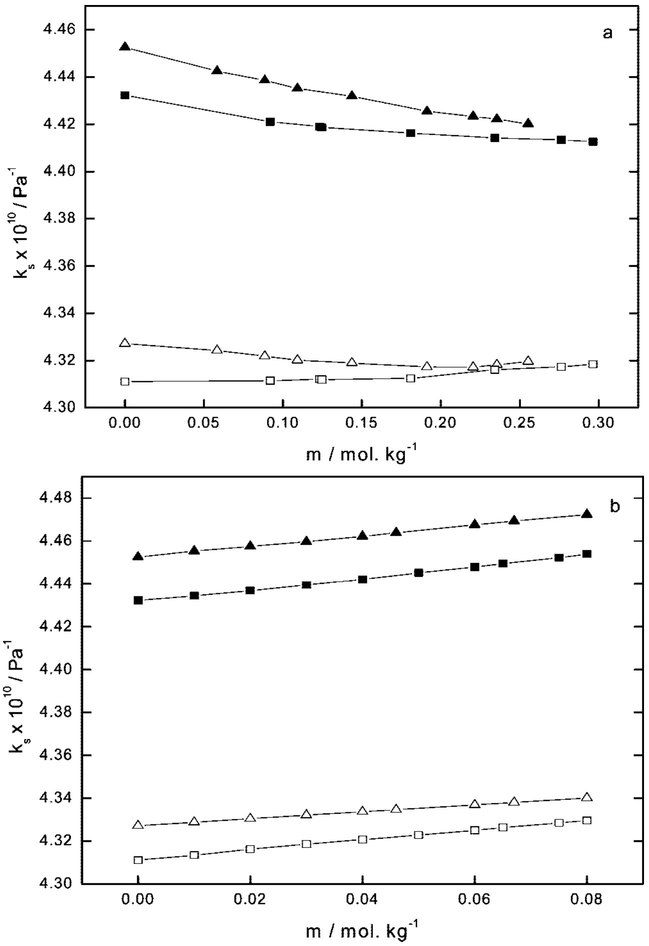

Figure 6. Isentropic compressibility, κ_s, of aqueous solutions of SDBS at different concentrations at 298.15 K: ▲, 0.05 mol·kg^{-1}; ■, 0.10 mol·kg^{-1}; and at 308.15 K: Δ, 0.05 mol·kg^{-1}; □, 0.10 mol·kg^{-1} with alcohols: (a) 1-pentanol and (b) 1-hexanol.

that $\Phi^{o}v$ values of 1-pentanol in aqueous SDBS are less than those in pure water at 298.15 K as $\Phi^{o}v_{(tr)}$ values are negative. However, for 1-hexanol, these values are positive at 298.15 K. The values of both $\Phi^{o}v$ and $\Phi^{o}v_{(tr)}$ increase with the increase in surfactant concentration for 1-pentanol as well as 1-hexanol. The sign of S_v is determined by the interaction between the solute species, and in the present study it is found to be positive as depicted in Table 3. No data could be found for the studied surfactant–alcohol solutions on studied thermodynamic properties for comparison.

Figure 5 illustrates the variation of the isentropic compressibility κ_s with concentration of aqueous SDBS. It shows a change in slope of κ_s vs $m^{1/2}$ with the change in the speed of sound at different temperatures. The results of the present studies of κ_s of aqueous solutions of SDBS containing 1-pentanol show a decreasing trend for different surfactant concentrations and temperatures except in the case of 0.10 mol·kg^{-1} aqueous SDBS at 308.15 K as shown in Figure 6a, whereas in the case of 1-hexanol in aqueous SDBS solution, the values of κ_s generally increase with an increase in concentration of alcohols for different surfactant concentrations and temperatures as is clear from Figure 6b. It may be due to the fact that 1-hexanol is more hydrophobic than 1-pentanol. The increase in the compressibility may arise because of the decrease in the structured water as a result of transfer of the additive alcohols from the aqueous phase to the micellar aggregates. This change is compensated by the loss of free space in the micelle interior upon addition of alcohols. It results in an increase in the compressibility of the micellar solutions. The decrease in κ_s as in the case of solutions containing 1-pentanol suggests that it is incompletely transferred from the aqueous environment to the micelle or it is located near the surface of the micelle. Generally, hydration makes a negative contribution to the compressibility of a solute, as

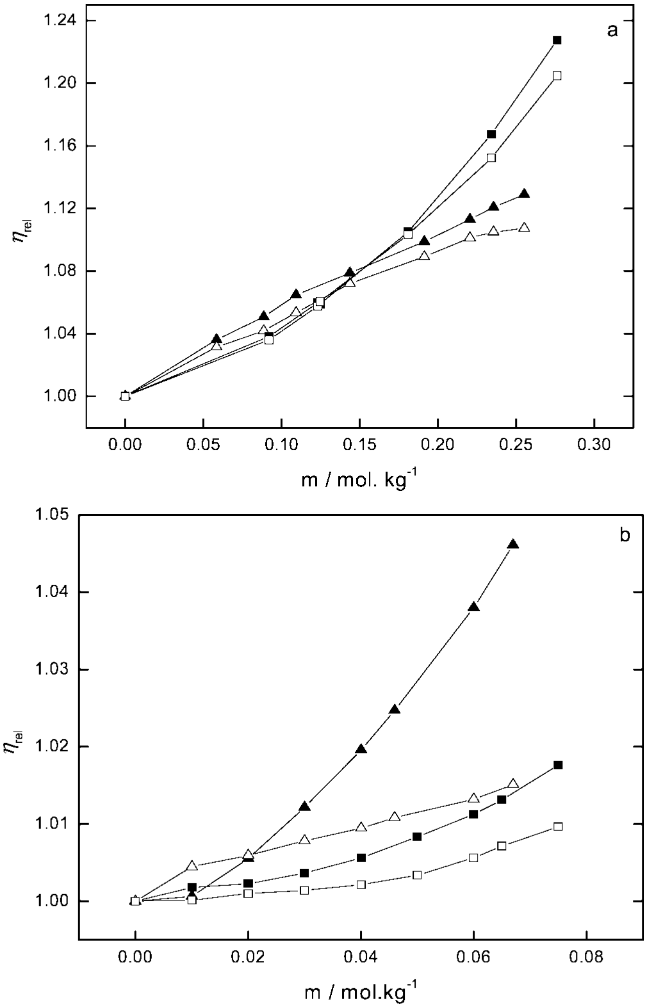

Figure 7. Relative viscosity of aqueous solutions of SDBS at different concentrations at 298.15 K: ▲, 0.05 mol·kg^{-1}; ■, 0.10 mol·kg^{-1}; and at 308.15 K: △, 0.05 mol·kg^{-1}; □, 0.10 mol·kg^{-1} with alcohols: (a) 1-pentanol and (b) 1-hexanol.

observed for monomeric surfactants as well as for simple electrolytes or their ions.[31]

The relative viscosities, at different molalities of aqueous SDBS, as a function of molal concentration of 1-pentanol and 1-hexanol, respectively, are presented in Figure 7. It can be seen from Figure 7a that η_{rel} in all the cases increases with the increase in concentration of alcohols and shows a clear break around (0.10 to 0.15) mol·kg^{-1} in the case of 1-pentanol. However, in the case of solution containing 1-hexanol (Figure 7b), no such trend could be found at the studied concentration range. Table 4 shows that *B*-coefficients are positive for 1-pentanol and 1-hexanol and increase with the concentration of SDBS from (0.05 to 0.10) mol·kg^{-1} and decrease with an increase in temperature from (298.15 to 308.15) K. However, an exception is found in solution containing 1-hexanol, where *B*-coefficients decrease with an increase in molal concentration of SDBS at 298.15 K. The *B*-coefficient measures the size and shape effects as well as the structural effect induced by solute−solvent interactions.[32] The positive values of *B*-coefficients are associated with structure making phenomena. The weak temperature dependence of *B*-coefficients of alcohols is similar to those obtained in pure nonaqueous solvents like methanol, acetonitrile, and ethanol.[16]

The ^{1}H NMR techniques have been frequently used to evaluate the micellar morphology in single as well as in mixed micelles.[17,32] The variation range of ^{1}H NMR chemical shift studies of solutions containing (0.05 and 0.10) mol·kg^{-1} SDBS and different concentrations of 1-pentanol are reported in Table 5. Typical spectra for 0.01 mol·kg^{-1} aqueous SDBS and the assignment of various peaks in the presence and in the absence of 1-pentanol (0.11 mol·kg^{-1}) are shown in Figure 8. In both the surfactant solutions, the chemical shift data for aryl protons (peaks a and b) show a small but consistent downfield shift with increasing concentrations of 1-pentanol. For the sake of clarity, the probable range of peaks *a* and *b* are presented in Table 5 as a_1, a_2, and b_1, b_2, respectively. A careful inspection of various ^{1}H signals in the case of pure surfactant solution and a shift in the position of these signals upon mixing 1-pentanol helps to deduce the preferential solubilization sites of 1-pentanol in aqueous SDBS solution. A comparison of the chemical shift (δ) of the proton spectra of aqueous SDBS solutions with that containing 1-pentanol clearly indicates the site for preferential solubilization of alcohol is the aromatic ring of the micelle unlike that in the case of aqueous SDBS solutions containing 2,6-di-*tert*-butyl-4-methylphenol (BHT) where it is solubilized within the hydrocarbon core of the micelle.[9] This is apparent from the significant change in frequencies of the aryl proton peaks (peaks

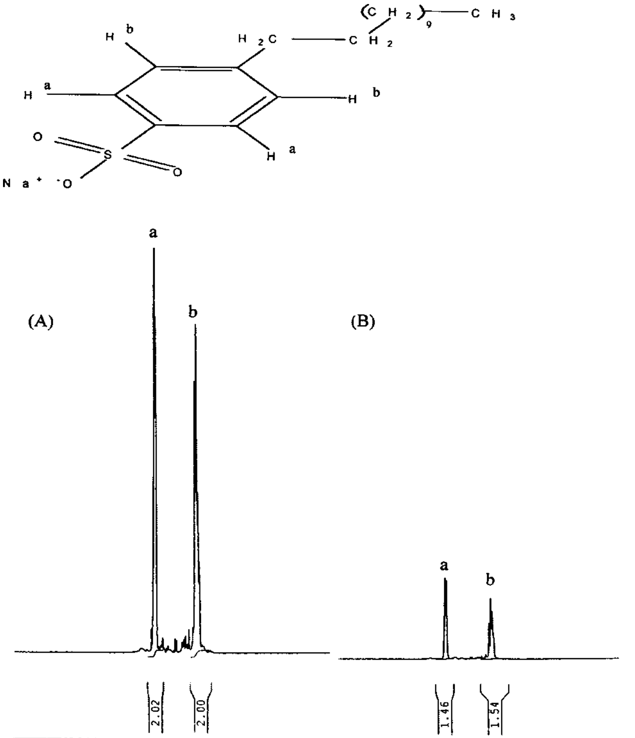

Figure 8. Structure of SDBS and ^{1}H NMR spectra in ppm at 295 K: (A) 0.10 mol·kg^{-1} SDBS and (B) 0.11 mol·kg^{-1} 1-pentanol in 0.10 mol·kg^{-1} SDBS in D$_2$O.

Table 5. Chemical Shift (δ) of Aryl Protons of SDBS Solutions in the Presence and in the Absence of 1-Pentanol in SDBS, (0.05 and 0.10) mol·kg^{-1}, at 295 K

SDBS *m*	1-pentanol *m*	variations range of aryl protons peaks/ppm			
mol·kg^{-1}	mol·kg^{-1}	a_1	a_2	b_1	b_2
0.05	0.0	7.5846	7.5688	6.9947	6.9747
	0.16	7.6233	7.6030	7.0399	7.0193
	0.20	7.6253	7.6050	7.0389	7.0200
	0.24	7.6293	7.6092	7.0388	7.0182
0.10	0.0	7.5879	7.5679	6.9874	6.9677
	0.11	7.6146	7.5962	7.0156	6.9968
	0.20	7.6227	7.6033	7.0271	7.0082
	0.23	7.6242	7.6046	7.0274	7.0074

a and *b*) of Figure 8. The chemical shift of methylene protons remains invariant. The peaks for the aliphatic protons of SDBS are overlapping with the peaks due to methylene protons of 1-pentanol which makes it impossible to comment about the shift in the position of aliphatic protons of NMR spectra. Moreover, the presence of a large number of aliphatic protons (25 protons) appearing over a narrow range of chemical shift makes their exact assignment unrealistic.

Conclusion

Various thermodynamic parameters for the studied aqueous SDBS solutions suggest that SDBS micelles undergo a second transition at higher surfactant concentration probably around $0.15\ \mathrm{mol \cdot kg^{-1}}$. The thermodynamic investigations for aqueous SDBS micellar solutions at different concentrations containing alcohols clearly indicate that the studied alcohol molecules behave as structure makers as concluded from viscosity *B*-coefficient values. In micellar solutions, these alcohol molecules are either incompletely transferred from the aqueous environment to the micelle, or it is located near the surface of the micelle as in the case of 1-pentanol except in the case of a solution of $0.10\ \mathrm{mol \cdot kg^{-1}}$ SDBS at 308.15 K. However, in solutions where 1-hexanol is present, the alcohol molecules seem to transfer completely from an aqueous environment to the micellar aggregates as concluded from the isentropic compressibility data. The positive $\Phi^{o}v$ values suggest the strong alcohol−surfactant interaction. The volumetric and viscometric studied are in good agreement with each other. The site for preferential solubilization of alcohol is the aromatic ring of the surfactant as concluded from ^{1}H NMR spectra.

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